IRON BUDGETS
IN
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ABSTRACT

Iron mass balances for eight lakes (76 lake-years of data) on the Canadian Precambrian Shield were measured including catchment, atmospheric and internal sources of iron. These data were compared to or combined with available data from the literature on iron fluxes in other North American and European Lakes. In most of these lakes, internal iron load was important; it resulted from anoxic sediment release since the 'lakes' hypolimnia became partly anoxic during summer stratification. Iron retention, based on external iron load only and determined from the ratio of incoming minus outgoing iron mass and incoming mass (R_{ext}), was correlated to internal load and not to morphometry and hydrology of the lake. On the other hand, when internal load was included in the calculated retention, (R_{tot}), retention was correlated with morphometry and hydrology, and not internal load. An average annual settling velocity of iron, computed from the relationship of R_{tot} with the annual water load (q_s), ranged from 12 to 26 m yr^{-1} depending on the data set.

A simple mass balance model was used to predict annual average iron concentration. Although model predictions and observed concentrations were significantly correlated, annual average concentrations were underestimated by the model in the Precambrian Shield lakes, but overestimated by atmospherically loaded and acid-stressed lakes from the Sudbury, Ontario region. Inclusion of a term related to organic acid content rendered the mass balance equation more general. Furthermore, the inclusion of dissolved organic acid concentration, colour of the lake water and loss on ignition of the surface sediment proved to be important secondary variables.

INTRODUCTION

Iron is an important element in lakes because of its chemical and biological interactions with other lake water constituents. It is an essential micronutrient for the phytoplankton and can control phytoplankton abundance when in short supply (Murphy 1983). Iron can also control the concentration and movement of nutrients like phosphate and toxic metals

(cadmium, lead, cobalt) in the water column (e.g., Sholkovitz and Copland 1982).

Its chemical properties are quite complex and change with the oxygen and organic carbon concentrations of the ambient medium. In the presence of oxygen and absence of organic acids, iron forms hydrous oxide particles that can adsorb other dissolved metals and phosphate; these particles can be sedimented to the lake bottom. The metals and phosphate remain adsorbed until oxygen is depleted and the redox potential of the medium changes. Under reducing conditions, the adsorbed species are dissolved and, depending on their chemical behavior, can be released into the anoxic water (either the pore water within the sediment or the anoxic hypolimnetic water), precipitate in the reduced state as sulfides or become adsorbed on insoluble iron sulfides (Gunkel and Sztraka 1986). Incidences of co-precipitation (Sholkovitz and Copland 1982), adsorption (Tessier et al. 1985) and co-migration of heavy metals and phosphate have been described before (Baccini and Joller 1981). Changes in the iron's redox state are also important in the study of acid lakes, as its reduction generates alkalinity (Psenner 1988, Cook et al. 1986).

Although the chemistry and adsorption properties of Fe have been studied extensively in the laboratory (e.g., Schnitzer and Kerndorff 1981, Liang and Morgan 1990) and field (Davis 1982), little is known about whole-lake and catchment fluxes. Few studies of whole-lake mass Fe balances have been done (see references in Table 3); in only one case, have iron budgets of more than one lake been reported (Dillon et al. 1988a). These five lakes, however, are quite extraordinary since they receive high inputs of strong acid, Fe and other metals from smelters in the Sudbury, Ontario area. Therefore, no generalizations have been made up to now about mass balances and iron fluxes in lakes.

In this study, we measured Fe mass balances of several lakes on the Canadian Precambrian Shield and pooled these data with all available quantitative information on Fe fluxes in other North American and European lakes. We present a general model using Fe budgets to predict annual Fe concentrations in a variety of lakes. In particular, we evaluated the predictive capability of a simple mass balance model similar to that used successfully for

phosphorus (e.g., Vollenweider 1968, Dillon and Rigler 1975). Next, the components of the mass balance model, such as retention, external and internal load, were investigated. Since the abundance of organic carbon influences the adsorption capacity and settling characteristics of iron hydroxides (reviewed by Mill 1980), we hypothesized that some of these Fe fluxes depend on input and concentration of organic acids measured as dissolved organic carbon (DOC), colour or organic content of the sediment (loss on ignition, LOI). Furthermore, we determined whether iron retention depends on lake morphometry and hydrology, as is the case for retention of other substances (e.g., phosphorus, Kirchner and Dillon 1975; nitrogen, DOC, Dillon and Molot 1990), and determined an average settling velocity from relationships of retention with hydrological characteristics.

Throughout our analysis, we separated the origin of the iron in lakes - either external sources such as runoff from the terrestrial catchment and atmosperic deposition on the lake's surface or internal sources such as the anoxic sediment surfaces. Mass balance equations and retentions are also calculated with explicit consideration of internal Fe load, and its importance is demonstrated.

MATERIALS AND METHODS

Description and symbols of the terms used in this study are summarized in Table 1.

Study Lakes

Iron mass balances were measured for eight lakes in south-central Ontario (45°-45°30'N, 78°-79°'W, Table 2). Budgets were measured for Blue Chalk, Chub, Dickie and Harp from 1978 to 1988, for Red Chalk from 1978 to 1979 and 1983 to 1988, for Plastic 1979 to 1988, for Crosson 1980 to 1988 and Jerry 1978 to 1980. Data are expressed on the basis of hydrological years, i.e., 1978 includes June 1, 1978 to May 31, 1979. In subsequent discussions, these lakes are termed the A lake data set.

A second set of study lakes (B lake data set) included 10 lakes (Table 2) for which Fe concentrations as well as morphometric and hydrologic data were measured as part of the study. These lakes were used to test several hypotheses described later.

A third set (C lake data set) consisted of lake data gleaned from the published literature (Table 3). This set included five lakes in the Sudbury area, Ontario (Dillon et al 1988a, Yan and Miller 1984) which experience substantial heavy metal pollution from local smelters. Data for eight additional lakes included two lakes in the Experimental Lake District (ELA) area, northern Ontario, two lakes from the Adirondacks of New York State, one more lake from the Canadian Shield, Ontario, and two European lakes. Data sets A and B offer the most reliable information because the data were usually collected over a long period (typically 10 or more years) and similar methods were used throughout. Therefore, emphasis is given to results based on these data sets. Data set C is used to test the generality of several of the hypotheses, although it should be considered that these iron budgets are based on one or two years only and the methods have not been evaluated in

detail but are different from those used by ourselves. Therefore, any differences in the results may be attributable to the methods as well as to different lake characteristics and geography.

Mass Balances

The discharges of all major inflows (2 - 6 per lake) and the outflows of each lake were monitored for the duration of the study; water level was continuously recorded at each site and converted to discharge using a site-specific stage-discharge relationship derived from 300-500 instantaneous measurements per site. Methods are described in detail in Locke and Scott (1984) and Scheider et al. (1983). The lake water budgets, including precipitation directly to the lakes' surfaces and lake evaporation estimated from meteorological data, balanced to within 5% in 76 out of 81 lake-years.

Each inflow or outflow was sampled 20 to 100 times per year for chemical analysis, with sampling more frequent during periods of high flow, especially the spring snowmelt period. The discharge data were integrated and combined with the concentration data to give estimates of the flux of Fe from each tributary into the lake and out of each lake via the lake's outflow. Flux of Fe into each lake from the portion of the lake's catchment that could not be gauged hydrologically (15 - 70%) was estimated by prorating the measured input from that lake's tributaries on an areal basis. The direct input of Fe to each lake in precipitation falling on the lake's surface was measured (Dillon et al. 1988, Jeffries 1984), combined with the input from the catchment and divided by the lake surface area (A_o) to yield external Fe loads L_{ext} (mg m^{-2} yr^{-1}). The mass leaving the lake via the outflow divided by A_o is called L_{out} (mg m^{-2} yr^{-1}).

Internal load (L_{int}), i.e., the load from internal Fe sources (the reduced sediment surfaces) was determined independently. The changes in the Fe mass of the whole water column during the stratification period, between June 1 and Oct. 31 in the lakes (June 1 to Sept. 30 in shallow Dickie Lake), were corrected for changes in the external input and output via

outflow during this period. Division by A_o then yields L_{int} (mg m^{-2} yr^{-1}). Since winter Fe release appeared to be very small (P. Dillon, unpubl. data), this estimate was considered applicable to the whole (hydrological) year. The total load, L_{tot} (mg m^{-2} yr^{-1}), is calculated as the sum of L_{ext} and L_{int}.

Fe retentions were computed from the mass balance data in two ways:

$$R_{ext} = (L_{ext}-L_{out}) / L_{ext} \qquad (1)$$

and

$$R_{tot} = (L_{tot}-L_{out}) / L_{tot} \qquad (2)$$

R_{ext} is the retention commonly estimated in lakes for various substances. It does not consider L_{int} and represents net retention including downward and upward fluxes. R_{tot}, on the other hand, includes L_{int} and can therefore be considered as gross retention based on downward fluxes only.

A simple one box mass balance model was applied to the data, similar to Dillon and Rigler (1975),

$$TFe = L_{ext} (1-R_{ext}) /qs \qquad (3)$$

or

$$TFe = L_{tot} (1-R_{tot}) /qs \qquad (4)$$

where q_s represents annual water load (m yr^{-1}). Both expressions are mathematically identical and they can be computed from the mass balance data by substituting Eq. 1 or Eq. 2 respectively into Eq. 3 or Eq. 4 to render Eq. 5.

$$TFe = L_{out}/qs \qquad (5)$$

Lake Concentrations of Fe

The concentration of Fe in each lake was measured 8 - 30 times per year. During the period of thermal stratification, volume-weighted samples were collected from the epi-, meta-, and hypolimnion by combining aliquots taken every 2 m. The resulting measured concentrations in the three strata were then combined in a volume-weighted manner to give a mean whole-lake concentration. Samples were collected throughout the entire water column when the lakes were homothermal. From these data, annual average whole lake Fe concentrations (TFe) were computed as the grand mean. Spring and fall Fe concentrations were calculated each as averages during the periods when the lakes were destratified.

Analytical

Fe concentrations in stream, lake and precipitation samples, DOC concentrations and water colour of the lakes were measured following methods outlined in detail in Ontario Ministry of the Environment (1983). LOI was determined with standard methods by igniting aliquots of the samples at 500° C to constant weight.

RESULTS AND DISCUSSION

Annual Average Iron Concentration (TFe)

TFe in the combined lake set (A,B and C data sets), ranged from 20 to 550 $\mu g\ L^{-1}$ (Table 4). All of the lakes with measured mass balances (A lakes) had TFe concentrations between 70 and 300 $\mu g\ L^{-1}$, while two B lakes and one lake from the data set C, polymictic Finjasjoen, exhibited concentrations of above 500 $\mu g\ L^{-1}$. Most of this iron is complexed with organic acids as long as it remains in oxic waters, since theoretically, iron concentrations at the prevailing freshwater conditions (pH > 4.8 and EH > 200 mvolt) can exceed 10 $\mu g\ L^{-1}$ only if complexed with organic acids (Mill 1980).

Concentrations of 30 $\mu g\ L^{-1}$ and below are typically found in lakes that develop hydrogen sulfide (H_2S) in their anoxic hypolimnia. In these lakes, H_2S precipitates ferrous iron as ferrous sulfide (FeS), forming a black layer above or in the sediment. The iron cycle in these H_2S containing lakes (Table 4) is different from the lakes where Fe out-competes H_2S. Retention of iron ought to be close to 100% due to FeS formation and biological uptake (Murphy 1983). There are no iron budget data available for these lakes probably because the analytical limits of establishing Fe budgets in such lakes will render any attempts difficult. For these reasons, this study concentrates on lakes with TFe above 30 $\mu g\ L^{-1}$. An exception to these lakes is Nelson Lake of the Sudbury region. Its low TFe concentration was artificially created by liming that reduced the TFe concentration from 61 to 20 $\mu g\ L^{-1}$ and is not due to FeS precipitation (Yan and Dillon 1984; Table 4).

Average annual TFe concentrations are highly correlated to spring turnover concentrations (r^2= 0.91, n=16, F-ratio=134) and t-test, and Wilcoxon's nonparametric test show no significant difference between the two (Fig. 1). On the other hand, fall turnover concentrations are significantly higher than TFe concentrations and the correlation is not as good (r^2=0.69, n=26, F-ratio= 54). Therefore, spring Fe concentrations may be substituted for annual TFe if annual average concentrations are not available, but not fall concentrations.

Mass Balances

External iron loads were highly variable (Table 5). Most of the external iron input stemmed from terrestrial sources for all lakes but the Sudbury lakes. Here, almost all of L_{ext} originated in anthropogenic sources, i.e., smelters, and entered the lake via precipitation directly on the surface. In the other lakes, much of the Fe entering the lake originated in the surrounding wetland areas and swamps and likely is associated with fulvic and humic acids (Devito et al. 1990). This view is strongly supported for the A lakes for which DOC budgets are available (P. Dillon, unpubl. data). Here, the correlation between annual external loads of DOC and Fe is highly significant (r^2= 0.85, n=76, $p<0.0001$, Fig.2).

Internal Fe load represents iron that originated in the sediment or on the sediment surface and that was released or dissolved when the oxygen was used up and the redox potential (EH) dropped to below 200 mvolt. Of the study lakes, all but Harp Lake exhibited significant hypolimnetic oxygen depletion during the summer. The average summer anoxic factors, which measure the extent of anoxia in space and time and represent the number of days an area equivalent to the whole lake surface area becomes anoxic (Nürnberg 1987), ranged between 13 and 27 days per summer for these lakes, and an average of 3.5 for Harp. All the EH values, except in Harp Lake, measured 1 m above the bottom in the late summer at a deep spot, were below 100 mvolt with the lowest (24 mvolt) in Blue Chalk Lake. L_{int} (Table 5) appears to be an important factor in the iron budgets; it is highly variable, independent of L_{ext} and can be up to four times larger than L_{ext} (Blue Chalk).

The iron loss via outflow (L_{out}, Table 5), used to calculate iron retention, is typically much lower than L_{ext} and never larger when the average L_{out} of several years is used, meaning that on average at least some loss of Fe to sediments occurs in all lakes. If individual years are considered, however, Chub, Crosson and Dickie each have more outflowing than incoming iron mass in two years, a phenomenon which can be explained by high sediment release of iron and high content of organic matter that keeps released Fe in suspension. DOC is indeed relatively high in these lakes (4-5 mg l^{-1}; Table 4).

The iron retentions (Table 5), R_{ext}, calculated on the basis of L_{ext} alone are lower than R_{tot}, based on the sum of L_{ext} and L_{int}, because if L_{int} is not considered, deceptively less iron appears to be retained in the lake. For the average of several years, R_{ext} remains positive but in the six cases (3 lakes for 2 years each) mentioned in the previous paragraph, it becomes negative when L_{out} is larger than L_{ext}. In the same years R_{tot} is still ca 0.60. R_{ext} in individual years ranges from -0.19 to 0.83, with an average of 0.43, while R_{tot} of individual years ranges from +0.19 to 0.98, with an average of 0.72. The sedimentation or gross retention as measured by R_{tot} depends on the morphometry and hydrology (w and q_s, Fig. 3 a, b). There is, however, no relationship of q_s or w with R_{ext}. Instead, R_{ext} is controlled by release from the sediment and is significantly correlated to L_{int} (for A lakes: n=8,

$r^2=0.58$, $p<0.003$; for all lakes without the significant outlier Finjasjoen: $n=15$, $r^2=0.39$, $p<0.013$, Fig 4). R_{tot} is not correlated to L_{int}. These results demonstrate the importance of considering iron release from sediment surfaces. If only the commonly used R_{ext} had been applied, the unconsidered influence of L_{int} on retention would have obscured its hydrological dependence.

Strong correlations of retention with q_s have been reported for several substances, especially for total phosphorus in lakes without internal phosphorus load, (i.e., where R_{ext} equals R_{tot} as in oxic lakes; Nürnberg 1984), and for the three nitrogen fractions, nitrate, ammonium and total nitrogen (Dillon and Molot 1990). The regression of the gross retention on the annual waterload can be used as a quantitative estimate for sedimentation, since

$$1/R_{tot} = 1 + 1/S \times q_s \qquad (6)$$

where S is the average mass transfer coefficient (m yr^{-1}, Dillon and Molot 1990) or settling velocity. Using all the available data without one outlier (Esthwaite), the equation is $1/R_{tot} = 1.18\ (0.087) + 0.054\ (0.015)\ q_s$ ($n=15$, $r^2=0.49$, $p< 0.003$, SE in parentheses, Fig. 5). The constant is indeed not significantly different from 1, and the reciprocal of the slope gives an average transfer coefficient of 18.5 m yr^{-1}; if forced through a constant of "1", settling velocity is 12.7 m yr^{-1}. For the A lakes, S is 10.5, ($1/R_{tot} = 1.06\ (0.15) + 0.095\ (0.029)\ q_s$, $n=8$, $r^2=0.64$, $p<0.017$). For the C data set only, including three Sudbury lakes, but without Esthwaite, S is estimated as 26.3; however, the constant is slightly higher than one ($1/R_{tot} = 1.17\ (0.006) + 0.038\ (0.009)\ q_s$, $n=7$, $r^2= 0.78$, $p< 0.009$).

The Fe transfer coefficient is similar to those determined for phosphorus which has been reported as 10 (Vollenweider 1975), 13.2 (Dillon and Kirchner 1975), 16 m yr^{-1} (Chapra 1975) or even higher (Nürnberg 1984). In low DOC lakes, the Fe settling velocity can be expected to be larger than the rate for P, since precipitation of oxidized iron occurs more rapidly than the biological sedimentation of P; in lakes coloured with dissolved organic matter, however, iron likely stays in solution even after aeration. In the clear hardwater

lakes Z$_T$ch and Constance, Sigg (1987) determined in sediment traps that summer sedimention of Fe was 2 and 4 times respectively larger than that of P on molar basis. The particle stability is an order of magnitude lower in these clear lakes (DOC < 1mg l^{-1}) than in coloured Swiss lakes (DOC 3-5 mg l^{-1}, O'Melia 1987), hence favouring sedimentation in clear lakes.

The dependence of retention on DOC or Colour in our study is supported by residual analysis of the model $1/R_{tot} = f(q_s)$. Without the literature lakes, there is a trend of increasing residuals with DOC (Fig. 6) and Colour. However, no trend of the residuals with internal load can be observed, suggesting that gross retention, i.e., sedimentation, is similar for both external and internal Fe load. The lower sedimention rate in the A lakes is likely the result of humic and fulvic acids.

Iron Mass Balance Model

A simple one box mass balance model (eq. 3, 4 or 5) was used to predict Fe concentrations in 15 A and C lakes. The computed iron concentrations ("L_{out}/q_s" in Table 5) are correlated to observed annual average iron concentrations (TFe, Table 4; Fig. 7a, $r^2 = 0.82$, n = 15, $p < 0.0001$). Model estimates for all but the Sudbury lakes are significantly lower than TFe (t-test, $p < 0.004$, n = 10); the deviation is 21% on average. Just as with the analogous phosphorus model that predicts ca 5% lower concentration (Dillon et al.1986), this deviation might be attributable to the assumption that the lake outflow and mid-lake concentrations of Fe are identical, an assumption inherent in the simple mass balance model. In fact, sedimentation during the passage between midlake and outflow may result in lower concentrations in the outflow. Apparently, Fe precipitation is more pronounced than P sedimentation. The Sudbury lakes' different behaviour, 67% ($p < 0.02$, n = 5) on average higher estimates, may reflect their different chemistry (very low DOC and pH), different source of iron (anthropogenic and airborne) and the chemical manipulations that several of these lakes have experienced. It appears that the atmospheric input between midlake station and outflow outcompetes the sedimentation within the lake; additionally, the

observed TFe concentration had been artificially reduced due to liming in at least two lakes (Table 4). Another possible explanation for the low settling velocity is the photochemical reduction of iron hydroxides to more soluble ferrous iron, as studied in laboratory experiments (Waite and Morell 1984) and observed in a clear acid mountain lake in Switzerland (Sulzberger et al. 1990).

The comparison of model estimates and measured TFe for up to 11 years each for the A lakes alone results in an average of 25% lower predictions ($n=100$, $p< 0.0001$, Fig. 7b). These TFe values also give an indication of the annual variation of the data. The year to year variation can be substantial (c.v. is mostly between 0.20 and 0.35), but is still lower than the lake to lake variation of TFe (c.v. 0.6) and its model in this data set. It can be concluded that the simple mass balance model gives proportionate, but not quantitative estimates of the average annual iron concentration. In lakes with natural iron sources, it tends to result in underestimates (similar to the phosphorus models), while in lakes with high airborne anthropogenic load, it tends to overestimate annual iron concentration. Since spring Fe concentrations are not significantly different from TFe data, they are correlated to the model estimates as well: $r^2= 0.95$, $n=8$, $p<0.0001$, with an average of 22% lower estimates (available for the A lakes only).

Effect of Organic Acids on the Fe Cycle

Before examining correlations of organic acid indicators on components of the Fe cycle, we present relationships of the indicators among themselves. Of DOC, colour and sediment LOI, DOC and colour are significantly correlated ($r^2= 0.50$, $n=18$, $p<0.001$, F-ratio= 16, Fig. 8). The regression is significantly improved, when lakes with TFe below 30 $\mu g\ l^{-1}$ are excluded ($r^2= 0.82$, $n=15$, $p< 0.0001$, F-ratio= 59). This means that in this subset of lakes, DOC and colour both indicate humic and fulvic acids. Sediment LOI, however, is neither correlated with DOC nor colour, which probably means it includes biomass and detritus.

Since dissolution and sedimentation of iron particles are influenced by dissolved organic matter, we examined if the mass balance model can be improved by inclusion of an organic matter term. We indeed found significant relationships of the residuals of the mass balance model with DOC concentration and LOI of the sediment for the combined data set including A and Sudbury Lakes (Fig 9). The addition of DOC to the mass balance model improves r^2 from 0.49 (n=13) to 0.90 and the F-ratio from 10 to 44 in TFe= -43.9 + 0.81 L_{out}/q_s + 30.0 DOC, n=13, p< 0.0001. The addition of LOI improves r^2 from 0.39 to 0.80 and the F-ratio from 6 to 18 in TFe= -190.7 + 1.07 L_{out}/q_s + 5.47 LOI, n=12, p<0.001. These significant multiple regressions for the data set including the Sudbury lakes mean, that the consideration of organic acids renders the model more general; it applies to lakes with natural tributary input as well as to lakes with anthropogenic airborne iron sources.

Considering TFe itself, we found several significant correlations with measures of organic matter. There was a strong correlation with colour for the A lakes: TFe = 53 + 6.5 colour, n=7, r^2= 0.80, p<0.007. When the remaining data or all data together are used, significant regressions including colour and q_s were obtained (r^2= 0.70, n= 11, p< 0.008 or r^2=0.67, n=18, p<0.0001). These good relationships with colour can be explained by the tendency of humic or fulvic acid to stain iron-rich water by keeping brownish iron oxyhydroxide particles in suspension that would otherwise (in clear waters) precipitate and settle to the bottom. Colour is in fact an indicator of iron and organic acids at the same time.

Like colour, DOC (r^2= 0.49, n=26, p<0.0001) and LOI (r^2=0.68, n=20, p<0.0001) are correlated to TFe in multiple regressions including q_s as an additional variable, again supporting our view that organic acids affect the iron cycle in lakes.

As described in the section on iron retention above, the residuals of the model $R_{tot}=f(q_s)$ have a tendency to follow a pattern with DOC, LOI and colour, but R_{tot} clearly is primarily controlled by morphometry and hydrology rather than organic acid indicators. Significant

relationships, however, exist for R_{ext}. Using all available data, it is correlated to both DOC ($r^2=0.55$, $n=13$, $p<0.004$) and LOI ($r^2=0.55$, $n=15$, $p<0.002$, Fig.10), probably reflecting a trend with L_{int}.

The many correlations of organic acid indicators presented here indicate the extent of organc acid interaction with iron. The consideration of DOC or LOI renders the mass balance model more general, and it applies even to acid lakes with anthropogenic Fe input. It can be concluded that DOC, colour and LOI serve well as indicators of humic and fulvic acids in these lakes.

CONCLUSION

This manuscript tries to evaluate quantitatively the iron cycle in natural lakes. While numerous kinetic and thermodynamic models for the chemistry and physics of different iron species in water exist (e.g., Stumm and Morgan 1981), many of these models fall short when trying to quantitatively describe the situation in real lakes. It is often impossible to determine all the concentrations and chemical activities of the constituents involved. Furthermore, the interaction with colloids is still little understood (Morel and Gschwend 1987). This work validates established, theoretical concepts and supports their applicability to real lakes. It presents a data base for future work that is intended to either fill the gaps in the empirical models with mechanistic experimentally tested models or to extend and validate the empirical relationships presented here.

This analysis is the first step to evaluate important constants (or variables), such as the average settling velocity of Fe and its dependence on organic acids, and to compare these dependencies and mass balances for numerous lakes. For example, the analysis of both retentions, the more commonly used R_{ext} and the here introduced R_{tot}, shows how important it is to consider internal load. Only R_{tot} demonstrates the expected dependency on hydrology and morphometry, while R_{ext} is controlled by L_{int}.

Many of the concepts and approaches have been borrowed from the studies of phosphorus cycling in lakes (e.g., Nürnberg 1984, Nürnberg 1991). It appears natural, that similar phenomena occur with substances that, like P and Fe, experience a redox controlled sediment release. Our empirical equations and the use of numerous slightly different variables should make it practical for other workers to compare and apply the equations to their own systems. For example, the management of drinking water impoundments can be facilitated by the application of our results. We hope that this study is most valuable in the comparison and quantitative evaluation of Fe and its cycling in lakes.

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Table 1 Symbols and definitions.

Symbol	Description
$\bar{z}$	Mean depth (m)
τ_w	Water residence time (yr)
q_s	Annual water load (m yr^{-1})
A_d	Watershed area (ha)
A_o	Lake surface area (ha)
Fe	Iron ($\mu g\ L^{-1}$)
TFe	Annual average whole lake total Fe ($\mu g\ L^{-1}$)
L_{ext}	External Fe load (mg $m^{-2}yr^{-1}$)
L_{int}	Internal Fe load (mg $m^{-2}yr^{-1}$)
L_{tot}	Total Fe load (mg $m^{-2}yr^{-1}$)
L_{out}	Output of Fe via lake outflow (mg $m^{-2}yr^{-1}$)
R_{ext}	Fe retention based on external load
R_{tot}	Fe retention based on total load
DOC	Dissolved organic carbon (mg L^{-1})
Colour	Average epilimnetic colour (Hazen Units)
LOI	Loss on ignition, organic content of sediment (%)

Table 2. Morphometric characteristics of the study lakes. A Lakes had Fe mass balances measured, B lakes had not. Symbols as in Table 1. na- data not available,

LAKE	A_d (ha)	A_o (ha)	$\bar{z}$ (m)	τ_w (yr)	q_s (m yr^{-1})
		A Lakes			
Blue Chalk	105.9	52.35	8.5	5.48	1.61
Chub	271.8	34.41	8.9	2.06	4.46
Crosson	521.8	56.74	9.2	1.67	5.71
Dickie	406.4	93.60	5.0	1.71	2.99
Harp	470.7	71.38	13.3	3.16	4.33
Jerry	861.0	50.10	12.4	1.25	9.99
Plastic	95.5	32.14	7.9	3.90	2.10
Red Chalk	na	57.13	14.2	2.63	5.57
		B Lakes			
Basshaunt	791.0	47.3	7.7	0.84	9.58
Bigwind	396.0	111.0	10.7	5.45	2.04
Buck	251.0	40.3	10.9	3.18	3.57
Glen	97.0	16.3	7.2	2.21	3.41
Gravenhurst Bay	790.0	179.4	9.8	3.60	2.71
Gullfeather	982.0	65.9	4.8	0.59	8.54
Little Clear	569.0	10.9	8.1	0.28	29.91
Paint-10	na	1.0	3.2	na	na
Solitaire	379.0	124.0	13.3	7.91	1.75
Walker	258.0	68.2	6.2	2.98	2.17

Table 3. Location and morphometrical characteristics of lakes from literature (C Lakes). All of the Sudbury lakes but Clearwater, had been limed in recent years. Symbols as in Table 1, na- data not available. Won., Wononscopomuc, deep and shallow basins. Key to references: 1- Cross and Rigler 1983; 2- Cook 1984; 3- Davison et al. 1980; 4- Löfgren 1987; 5- Nürnberg 1984 b, c; 6- Lee 1962; 7- Dean and Greeson 1979; 8- Effler et al. 1981; 9- Schindler et al 1976; 10- Nürnberg 1987; 11- Dillon et al. 1988a, Yan and Dillon 1984.

LAKE	Lat.	Long.	A_o (ha)	$\bar{z}$ (m)	τ_w (yr)	q_s (m yr^{-1})	Reference
Bob	44 55'N	78 47'W	228	18.0	2.99	6.02	1
Lake 227 (ELA)	49 41'N	93 40'W	5	4.4	2.15	2.05	2
Esthwaite	54 21'N	3 00'W	100	6.4	0.25	25.60	3
Finjasjoen*	56 08'N	13 42'W	1110	3.8	0.33	11.51	4
Jack's	44 41'N	78 02'W	na	8.8	8.00	1.10	5
Magog	45 18'N	72 03'W	1044	9.8	0.06	163.33	5
Memphramagog	45 05'N	72 15'W	280	10.0	na	na	5
Mendota	45 30'N	89 25'W	3910	12.4	5.50	2.26	6
Oneida*	43 15'N	76 00'W	20700	6.8	0.67	10.15	7
Onondaga	43 00'N	76 10'W	1170	12.0	0.27	44.44	8
Rawson (ELA)	49 40'N	93 45'W	54	10.5	6.35	1.65	9
St.George, East	43 57'N	79 25'W	5	5.5	2.30	2.40	5
St.George, West	43 57'N	79 25'W	4	5.2	2.16	2.40	5
Waramaug	41 30'N	73 22'W	272	7.0	0.83	8.43	10
Won., deep	41 45'N	73 20'W	70	12.5	4.00	3.12	10
Won., shallow	41 45'N	73 20'W	24	8.5	4.00	2.12	10

Sudbury Lakes

Clearwater	46 22'N	81 03'W	76.5	8.3	4.40	1.89	11
Hannah	46 27'N	81 02'W	27.3	4.0	3.00	1.33	11
Lohi	46 23'N	81 02'W	40.5	6.2	1.30	4.77	11
Middle	46 26'N	81 02'W	28.2	6.2	1.80	3.44	11
Nelson	46 44'N	81 05'W	309.0	11.6	9.30	1.25	11

*polimictic, not stratified

Table 4. Average annual whole lake iron concentration (TFe), pH, organic carbon (DOC and color) and loss on ignition of the surface sediments. Symbols as in Table 1, na- data not available. Data correspond to the years for which budgets are available, whenever possible.

Lake	TFe ($ug\ l^{-1}$)	pH	DOC ($mg\ l^{-1}$)	Color (Hazen)	LOI (%)
		'A' and 'B' Lakes			
Blue Chalk	70	6.61	1.79	5	33
Chub	273	5.62	4.74	33	50
Crosson	263	5.58	4.06	23	41
Dickie	276	5.80	5.10	35	37
Harp	106	6.28	3.86	20	34
Jerry	213	6.09	4.76	na	38
Plastic	106	5.73	2.24	5	42
Red Chalk	120	6.32	2.49	9	41
Basshaunt	80	6.68	4.16	24	na
Bigwind	100	6.33	3.17	9	na
Buck	120	6.49	2.82	5	41
Glen*	30	7.70	3.78	8	na
Gravenhurst Bay	162	7.00	3.60	na	28
Gullfeather	550	5.90	5.14	51	na
Little Clear	520	6.58	2.66	10	45
Paint-10	200	5.30	4.30	20	61
Solitaire	40	6.58	2.11	5	37
Walker	70	6.55	3.69	10	15

'C' Lakes					
Bob	na	6.67	na	na	30
Dart's	na	5.10	na	na	na
Lake 227 (ELA)	na	6.20	na	18	48
Esthwaite	na	na	na	na	24
Finjasjoen	550	8.90	na	na	na
Jack's*	20	7.00	na	11	na
Magog	140	7.50	na	na	na
Memphramagog	35	7.50	na	na	na
Mendota	na	7.00	na	na	na
Oneida	36	8.10	na	na	na
Onondaga	na	na	na	na	na
Rawson	na	6.20	na	na	31
St.George, East*	20	7.40	6.50	24	32
St.George, West*	20	7.40	7.60	25	28
Waramaug	na	6.40	3.70	na	23
Wononscopomuc*	20	7.00	3.00	na	31
Won., shallow*	20	6.90	2.80	na	32
Sudbury Lakes					
Clearwater	88	4.40	0.50	na	20
Hannah	169†	6.70	0.50	na	20
Lohi	72†	4.75	0.50	na	24
Middle	106†	6.70	0.50	na	28
Nelson	20†	6.70	0.50	na	na
mean	144	6.5	3.24	17.6	34
Range	20 - 550	4.4 - 8.9	0.5 - 7.6	4.6 - 51.4	15 - 61

SE (% of mean)	26.5	0.14	0.34	2.76	2.0

*Hydrogen sulfide lakes

†Pre-liming concentrations: Hannah 104, Lohi >90, Middle na, Nelson 61.

Table 5. Iron budget data. Averages of annual observations for specified years are presented (Years). Symbols as in Table 1. All loads in mg $m^{-2}yr^{-1}$, L_{out}/q_s, model of eq. 5; na- data not available.

LAKE	L_{ext}	L_{int}	L_{out}	L_{out}/q_s	L_{tot}	R_{ext}	R_{tot}	Year
				'A' Lakes				
Blue Chalk	269	1043	81	50	1311	0.68	0.94	78-88
Chub	1109	1597	881	194	2706	0.18	0.65	78-88
Crosson	1322	1635	1198	210	2963	0.08	0.51	80-88
Dickie	1021	1182	621	207	2204	0.34	0.71	78-88
Harp	1266	0	456	103	1266	0.64	0.64	78-88
Jerry	2735	295	1407	142	3030	0.48	0.53	78-79
Plastic	501	883	239	110	1384	0.52	0.83	79-88
Red Chalk	862	891	464	81	1753	0.45	0.74	78-79, 83-88
				'C' Lakes				
Clearwater	1856	0	363	192	1856	0.80	0.80	77
Hannah	894	0	242	182	894	0.73	0.73	77
Lohi	1620	na	770	161	na	0.52	na	77
Middle	1525	na	567	165	na	0.63	na	77
Nelson	485	0	74	59	485	0.85	0.85	77
Bob	4209	0	985	164	4209	0.77	0.77	75
ELA-227	1431	8932	na	na	10363	na	na	79
Esthwaite	20000	2700	6400	250	22700	0.68	0.72	78
Finjasjoen	6500	8514	5455	474	15014	0.16	0.64	82-83
Mendota	239	na	46	20	na	0.81	na	49

Oneida	974	0	386	38	974	0.60	0.60	79
Onondaga	45236	na	na	na	na	na	na	69,75
Rawson	647	0	94	57	647	0.85	0.85	72-73
Mean	4510	1628	1091	150	4339	0.57	0.72	
Range	239 -	0 -	46 -	20 -	485 -	0.08 -	0.51 -	
	45235	8932	6400	474	22700	0.85	0.94	
SE (% mean)	2239.4	674.9	402.5	23.7	1472.9	0.054	0.030	

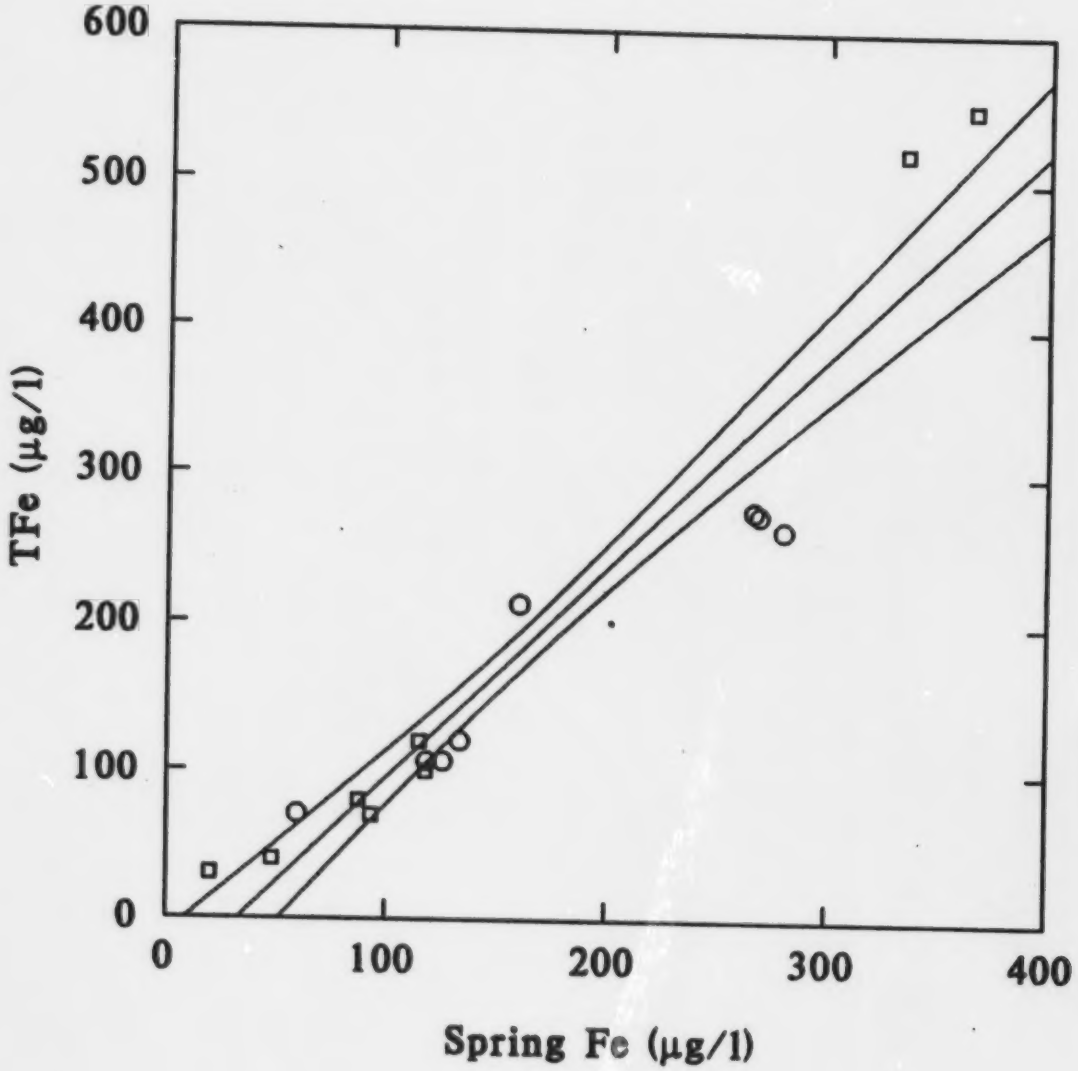


Figure 1

Figure 2

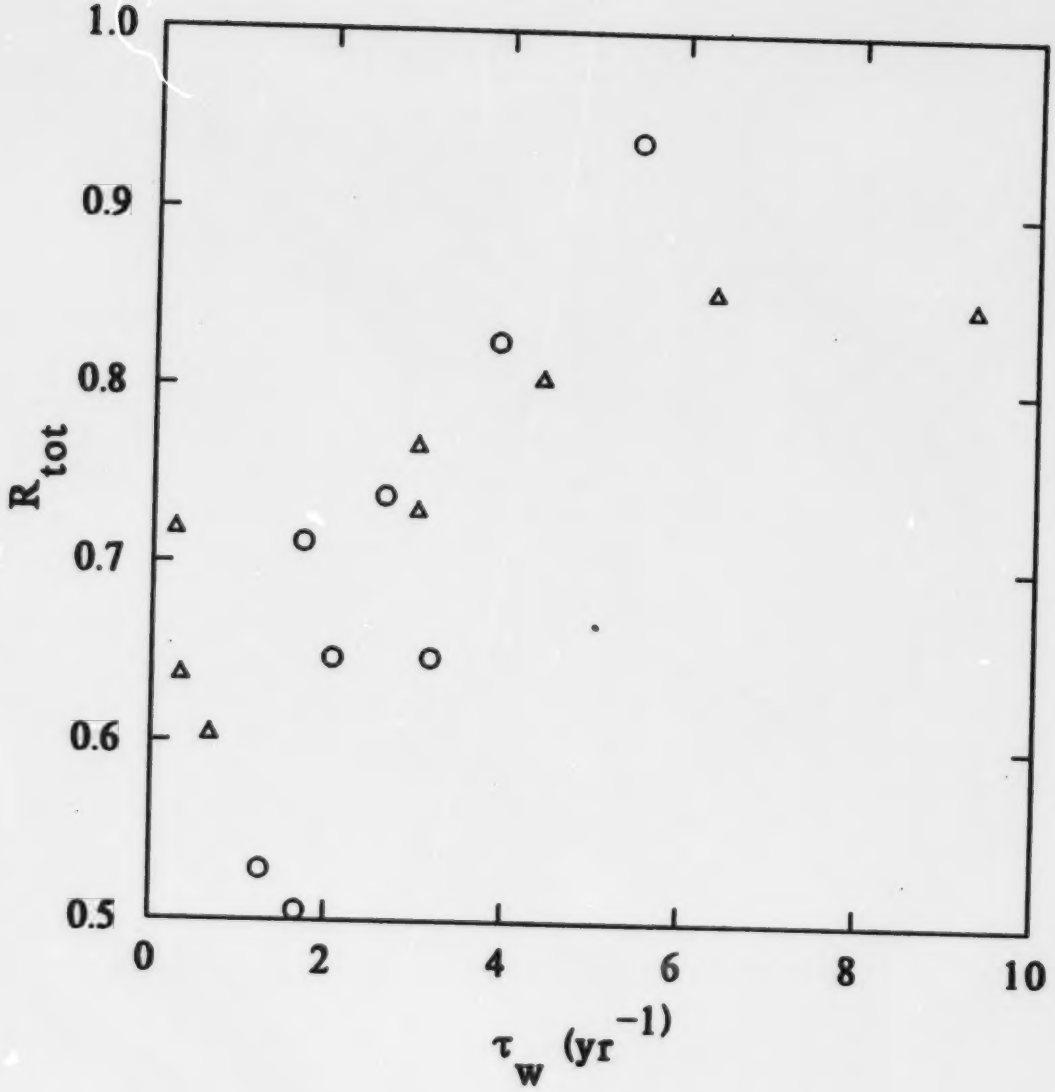


Figure 3a

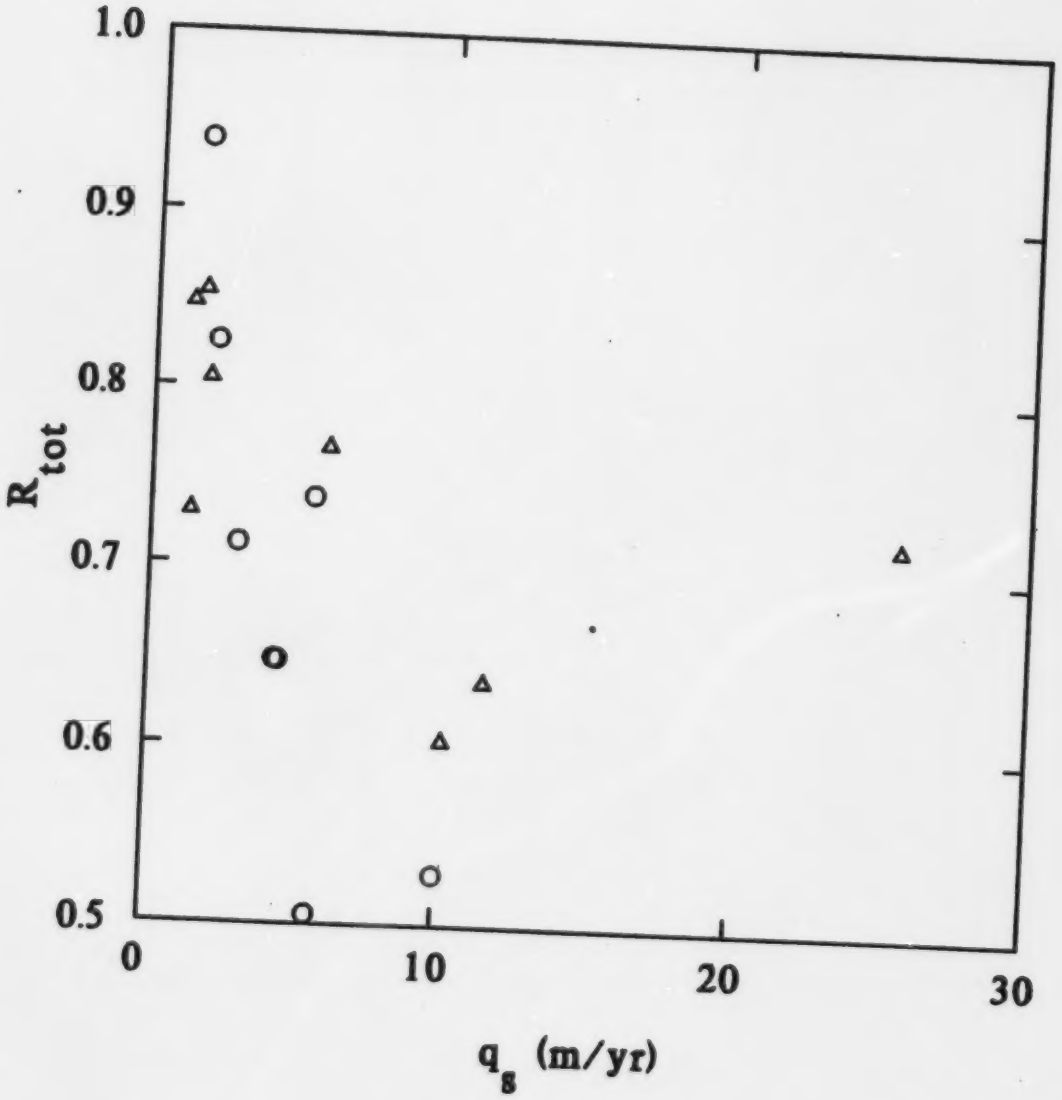


Figure 3b

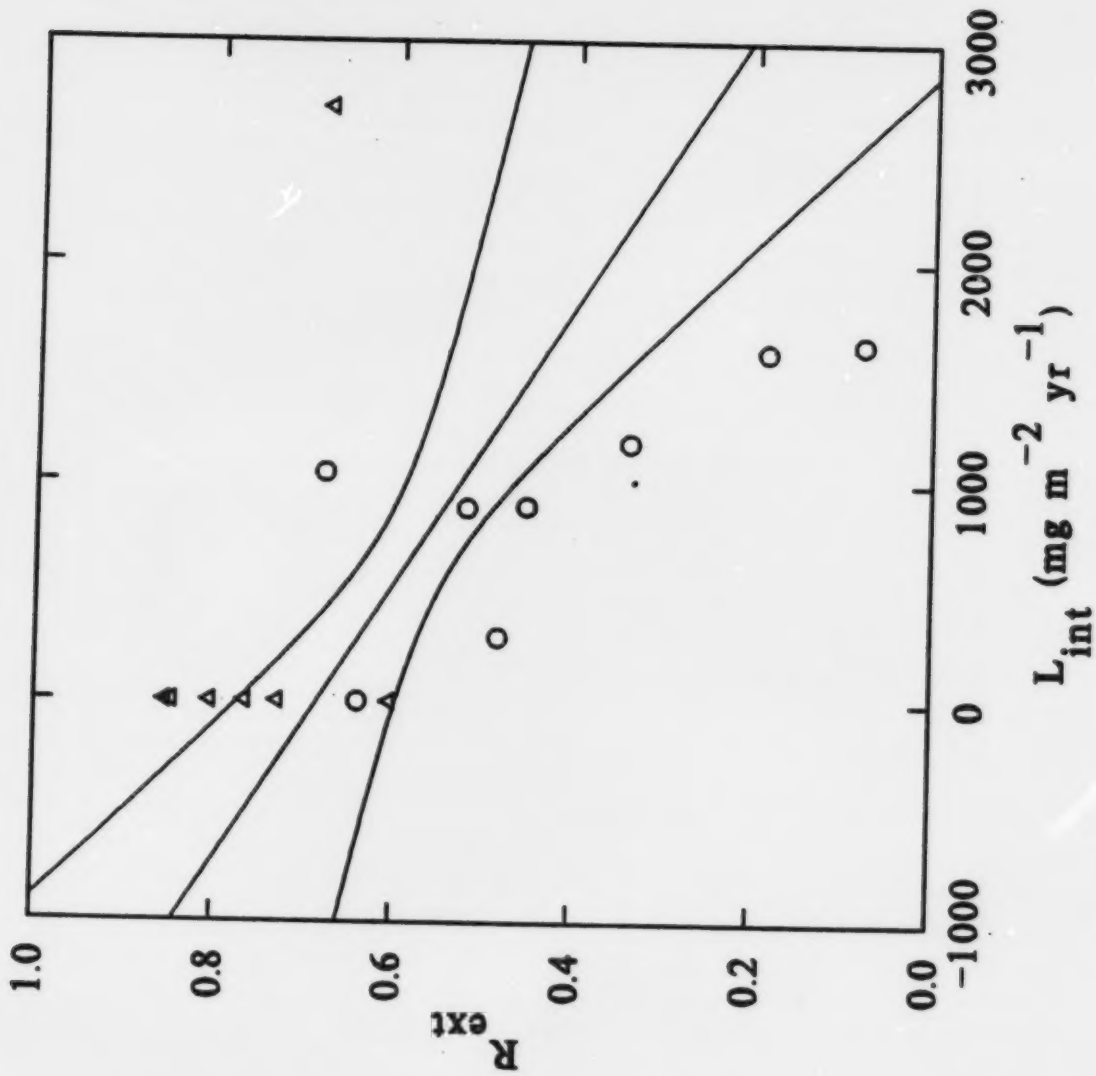


Figure 4

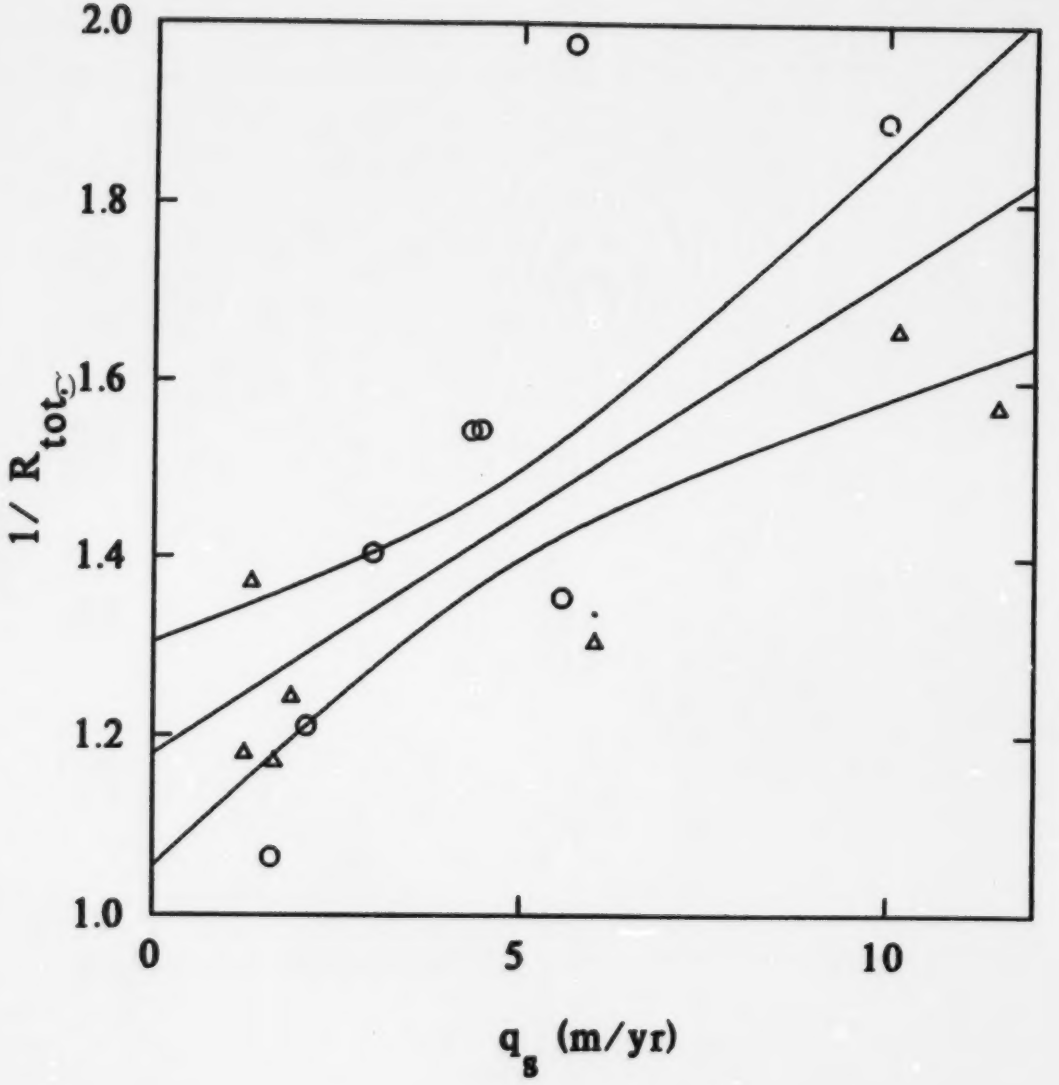
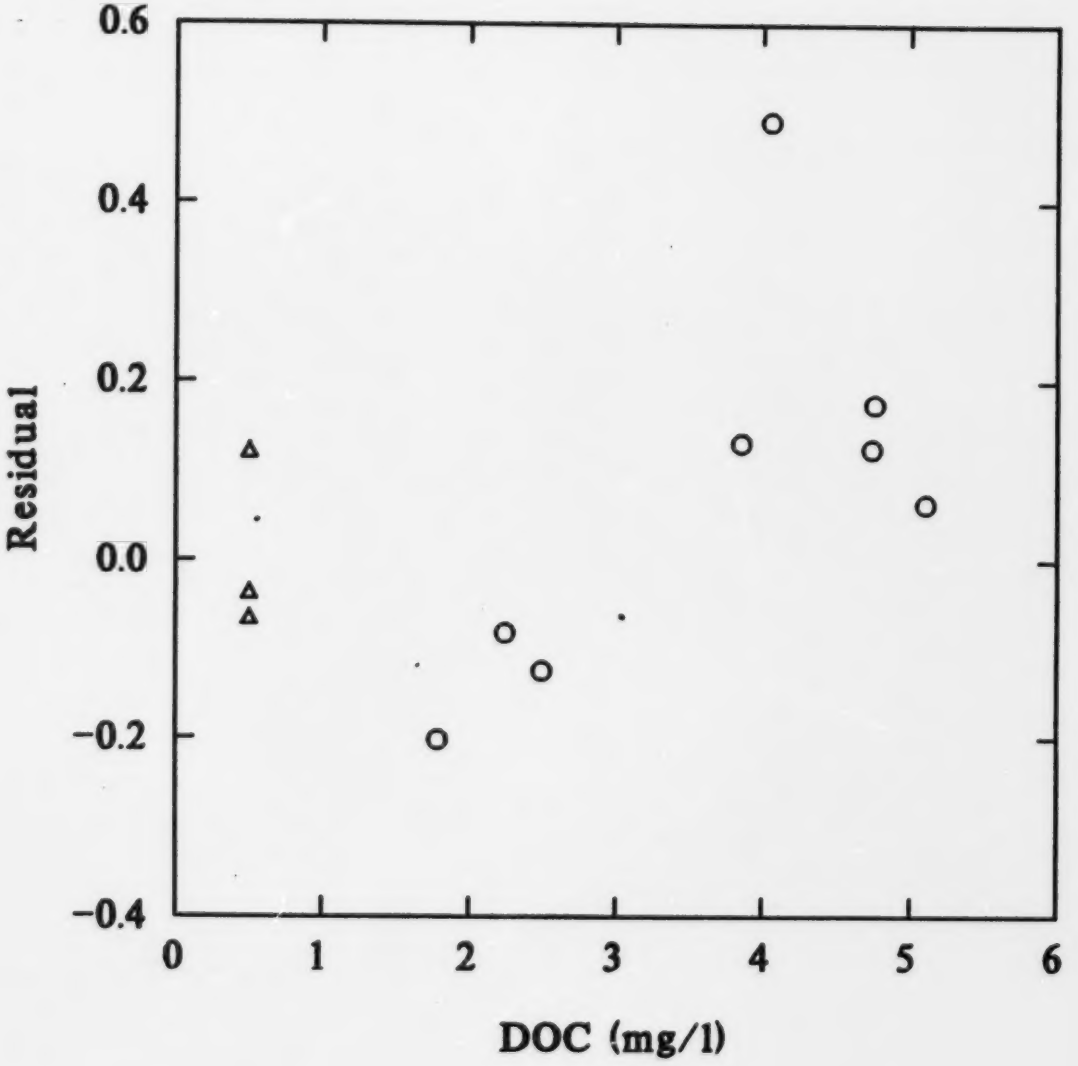


Figure 5



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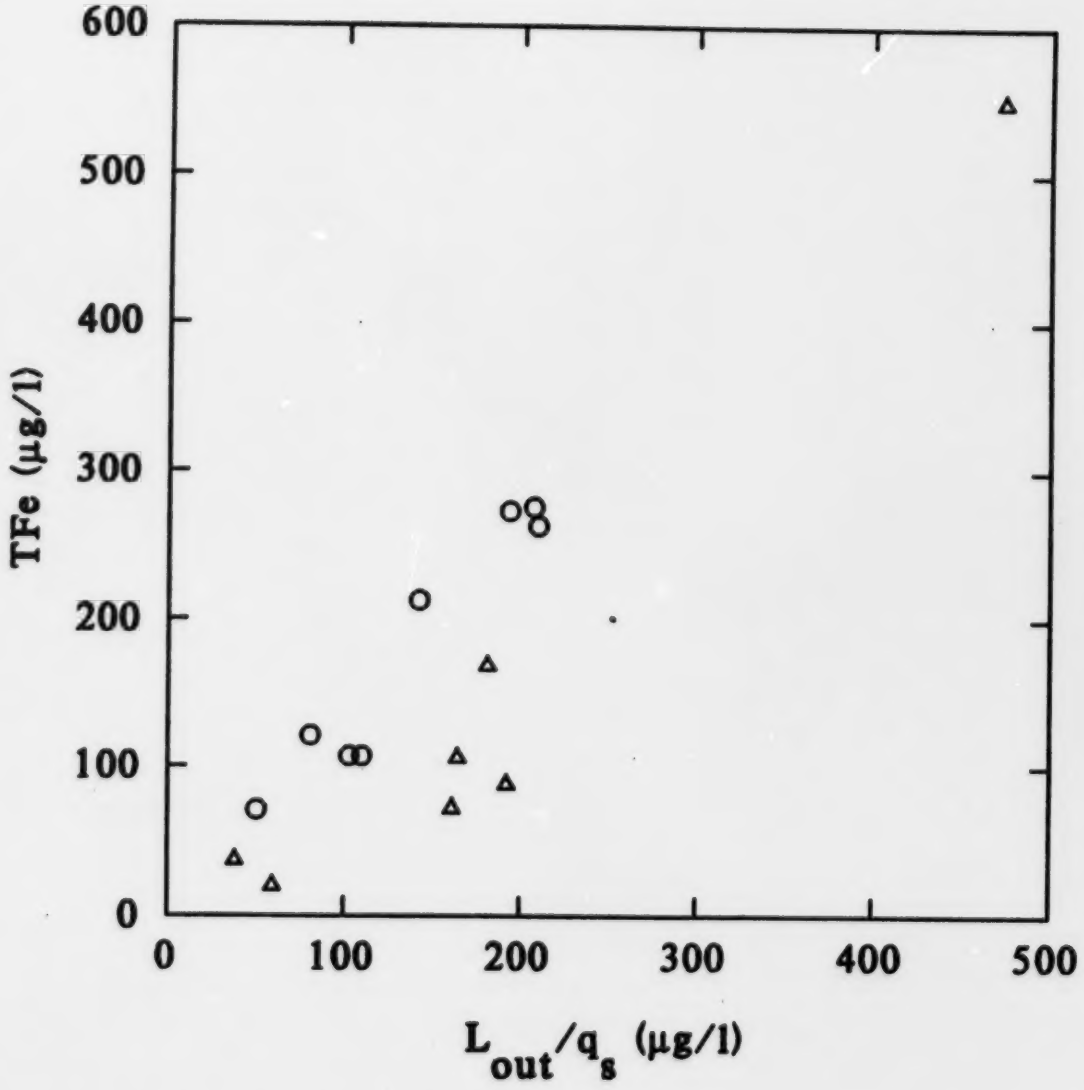
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400
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200
100
0
TFe (µg/l)
0
100
200
300
400
500
L_{out}/q_s (µg/l)

Figure 7a

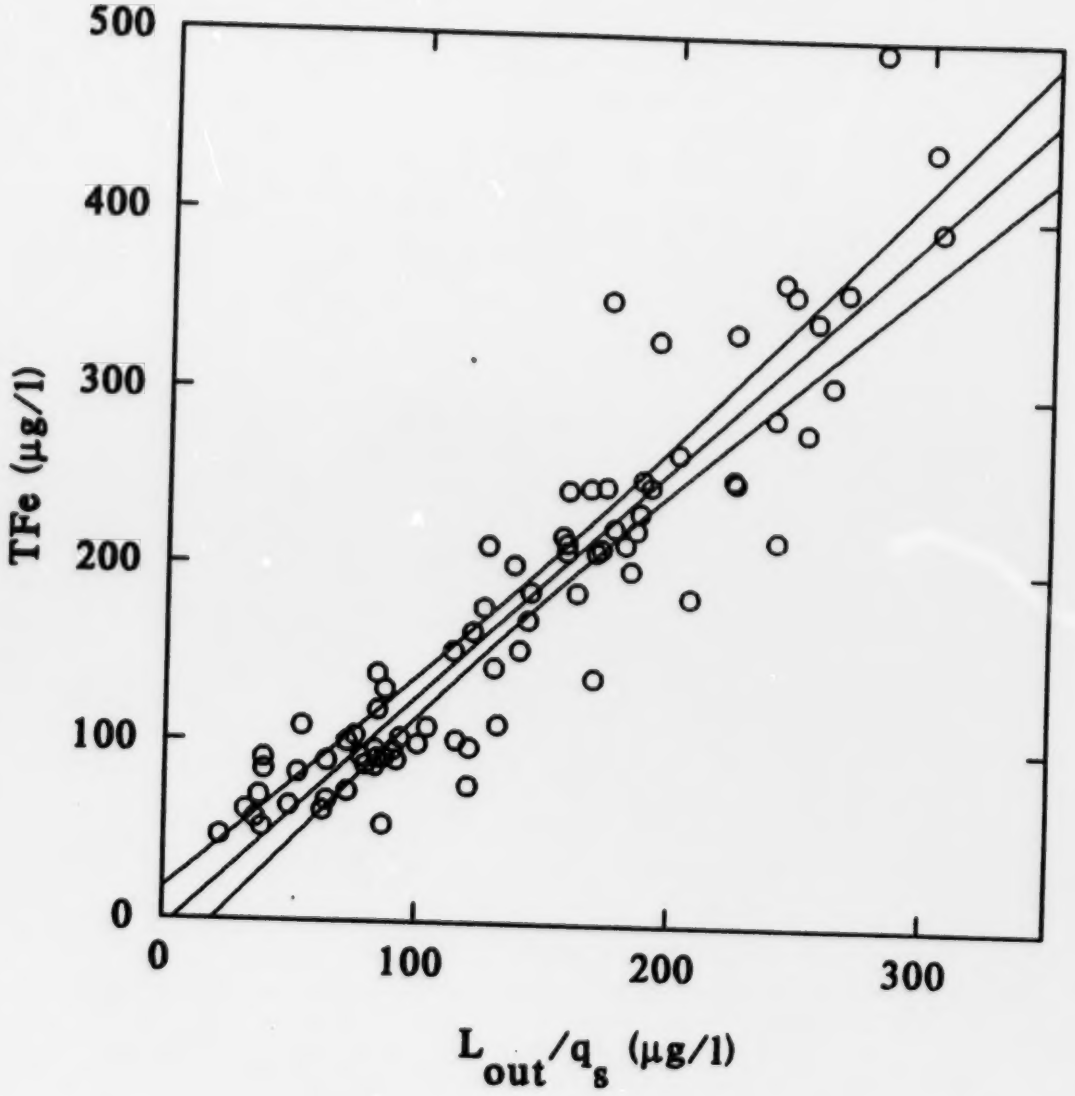

Figure 7b

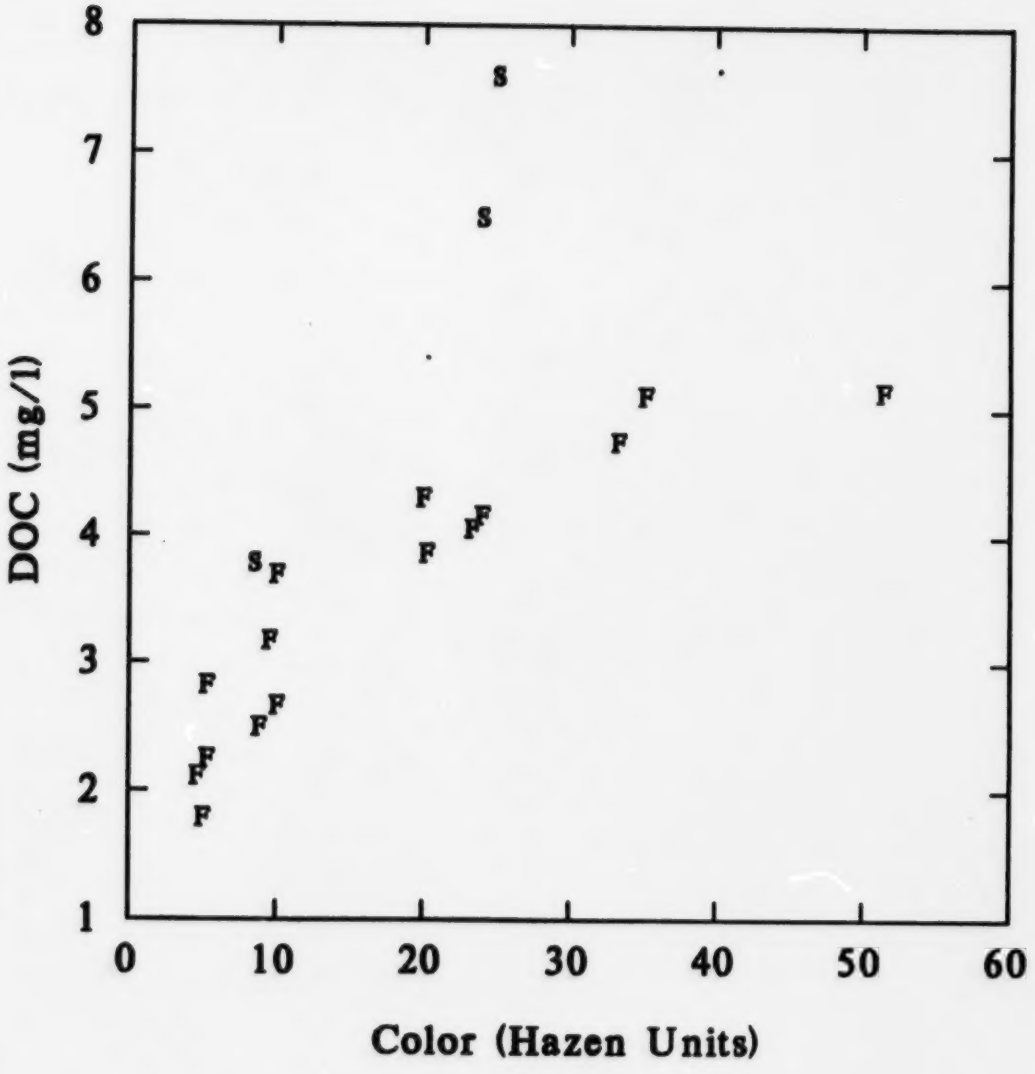
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Figure 8

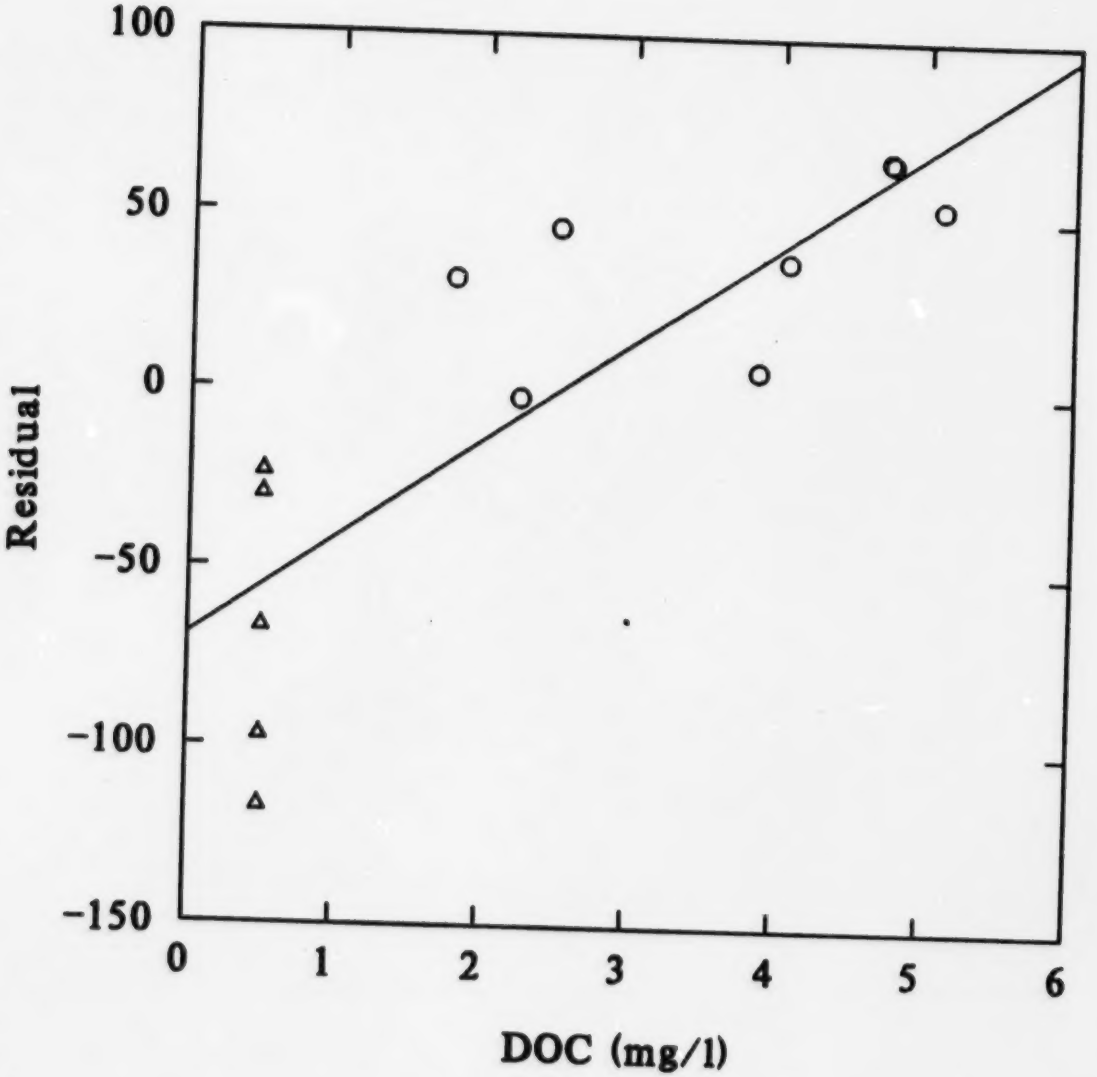

Figure 9a

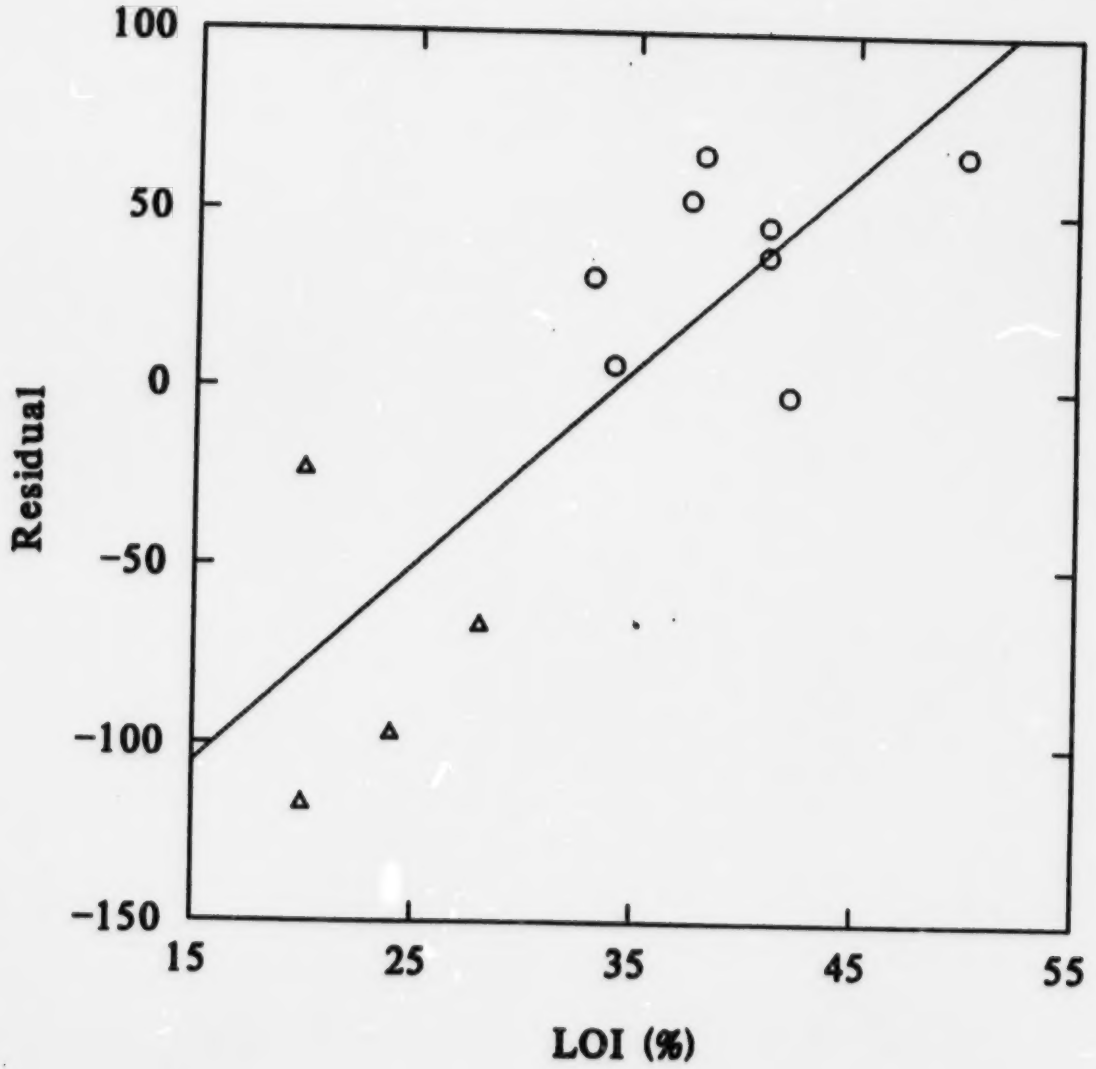

Figure 9b

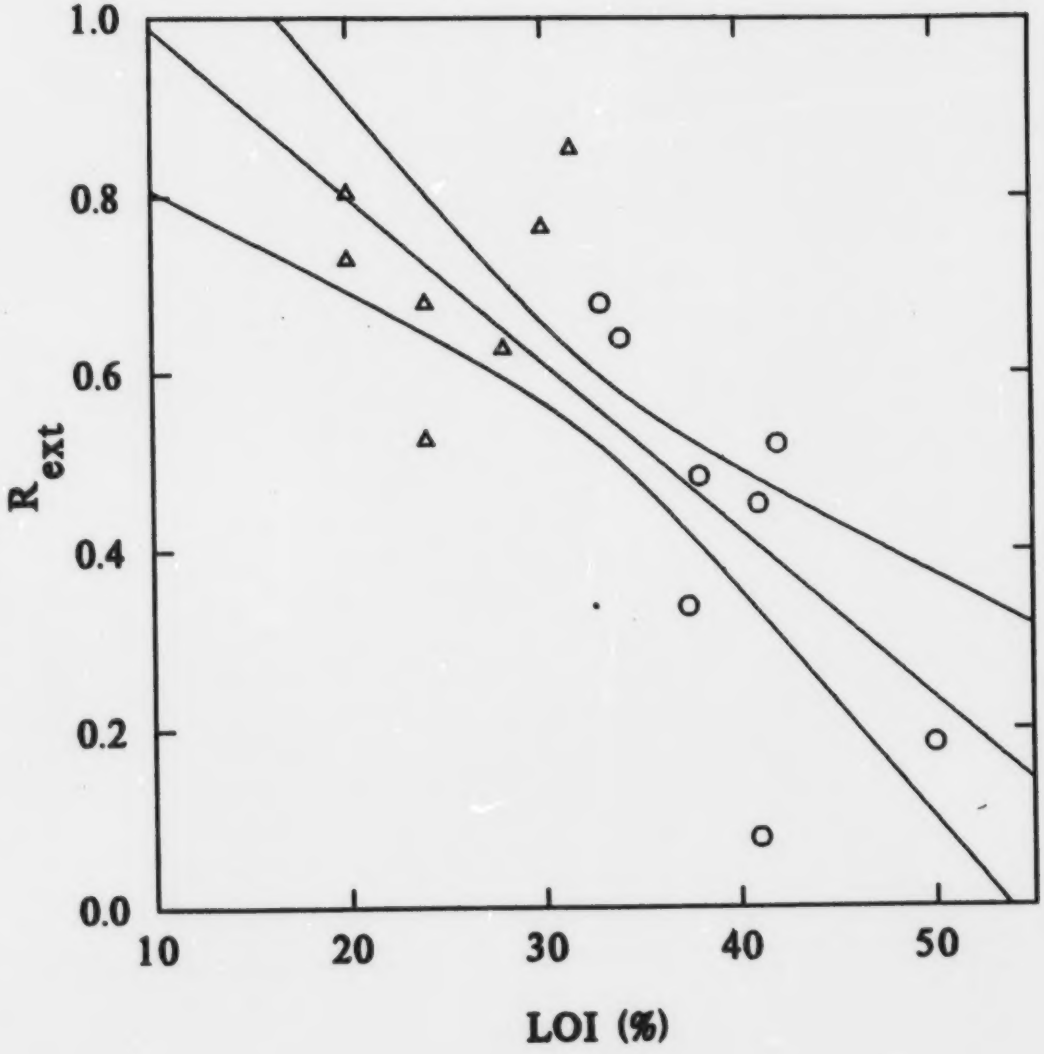

Figure 10